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Reactions of Metal Carbonyls with the Azide Anion [1]

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The kinetics of the reaction of metal hexacarbonyls $M(CO)_6$ ($M = Cr, Mo, W$) with tetraethylammonium azide in acetone solution have been studied in detail. The ionic reaction products $NEt_4[M(CO)_5NCO]$ are formed by an S_N2-type mechanism suggesting a primary, rate-determining attack of the azide anion to the carbon atom of a CO group. The activation energy for this step depends on the metal hexacarbonyl and decreases in the order $Cr > Mo > W$. The preparation of the azido complex $[As(C_6H_5)_4][W(CO)_5N_3]$ together with some preliminary results on the reactions of other metal carbonyl compounds, e.g. *$Mn(CO)_5Br$, $Re(CO)_5Cl$, $Co_2(CO)_8$ and $Fe(CO)_5$, with the azide ion are reported.*

Introduction

The metal hexacarbonyl compounds of the group VIb elements react with tetraalkylammonium azides even under very mild conditions (*e.g.*, at 20-50° in diglyme or acetone) to give the anions $[M(CO)_5NCO]^-$.[2,3]

$$M(CO)_6 + NR_4N_3 \longrightarrow NR_4[M(CO)_5NCO] + N_2 \qquad (1)$$

For M = W, preliminary kinetic studies showed a first-order rate dependence on both the hexacarbonyl and the azide concentrations, thus supporting a mechanism analogous to that of the Curtius reaction of acyl azides.[3] In continuing this work, we have also investigated the kinetics of the reactions of $Cr(CO)_6$ and $Mo(CO)_6$ with N_3^- at different temperatures. The present paper summarises the kinetic data and gives some further comments to the reaction mechanism. In addition, some preliminary results on reactions of other metal carbonyl compounds with the azide anion are described.

Experimental Section

All operations, except the handling of some of the solid complexes, were carried out in a pure nitrogen atmosphere. The solvents were dried over P_2O_5 (acetone) or CaH_2 (diglyme, tetrahydrofurane) and preserved in a steady-distillation apparatus from which they could received immediately before use.

Reactions of $M(CO)_6$ ($M = Cr, Mo, W$) and $N(C_2H_5)_4N_3$. The preparation of the compounds $[N(C_2H_5)_4][M(CO)_5NCO]$ (M = Cr, Mo, W) used to determine the exact intensities of the infrared absorptions was reported by us previously.[2,3] Under the experimental conditions employed for the kinetic runs, the reactions of the chromium and tungsten hexacarbonyls and azide give a practically quantitative yield of the $[M(CO)_5NCO]^-$ anions.[4] The reaction of molybdenum hexacarbonyl with the azide give the corresponding pentacarbonyl isocyanato anion as the major but not as the only reaction product. In addition, small amounts of another pentacarbonyl, possibly $[Mo(CO)_5N_3]^-$, are formed together with a fairly air-sensitive compound of approximate composition $[N(C_2H_5)_4]_3[Mo(CO)_3X_3]$ ($X = N_3$, NCO). The infrared spectrum of this compound shows two C–O stretching frequencies at 1870 and 1730 cm^{-1} indicating the presence of a *cis*-$Mo(CO)_3$ group.

Determination of Rates. The techniques used for the kinetic measurements were the same as described in our previous paper.[3] At zero time the prethermostated solutions of the starting compounds $M(CO)_6$ and $N(C_2H_5)_4N_3$ were mixed in a Schlenk tube and transfered immediately into the infrared cell which was kept by a thermostated jacket at the reaction temperature. Because of the low solubility of the tetraethylammonium azide in acetone, ligand concentrations were limited to approximately $3.5 \times 10^{-3}\,M$. The spectra of the reacting solutions were recorded in the region 2100-1850 cm^{-1} at regular time intervals. The reaction rates were determined by following the decrease in intensity of the C–O stretching frequency of the hexacarbonyl and, for M = Cr, W, also by following the increase in intensity of the νC–O absorptions of the $[M(CO)_5NCO]^-$ anion. The data gave good linear plots of log $\dfrac{[A]_0[B]_t}{[A]_t[B]_0}$ *vs.* time (where $[A]_0$, $[A]_t$ are the concentrations of $M(CO)_6$ and

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[1] (a) Part X in the series: Kinetic studies of substitution reactions of metal complexes. Part IX: E. Deckelmann and H. Werner, *Helv. Chim. Acta, 52,* 892 (1969); (b) Part XXVIII in the series: Pseudohalogenometal complexes. Part XXVII: W. Beck, W. P. Fehlhammer, P. Pöllmann, and H. Schächl, *Chem. Ber. 102,* 1976 (1969).

[2] W. Beck and H. S. Smedal, *Angew. Chem. 78,* 267 (1966); *Angew. Chem. internat. Edit. 5,* 253 (1966).

[3] W. Beck, H. Werner, H. Engelmann, and H. S. Smedal, *Chem. Ber. 101,* 2143 (1968).

[4] We did not investigate the solvent dependence of the rate of reaction (1) but were informed by Prof. F. Basolo, Northwestern University, Evanston, that one of his coworkers studied the kinetics of the reaction of $W(CO)_6$ and N_3^- in different solvents. We thank Prof. Basolo for this information.

$[B]_o$, $[B]_t$ the concentrations of $N(C_2H_5)_4N_3$ at time zero and t) for at least up to 80% completion of the reaction. The average deviation of the rate constants for identical runs was almost always less than 5%.

Preparation of $[As(C_6H_5)_4][W(CO)_5N_3]$. 0.6 g (1.7 mmole) $W(CO)_6$ dissolved in 40 ml tetrahydrofurane were irridiated with a TQ 81 Hanau quartz lamp until 38 ml (1.7 mmole) CO were evolved. The yellow solution was treated with 0.3 g (1.9 mmole) $N(C_2H_5)_4N_3$ in 30 ml acetone in the dark. After filtration, the solvent was removed in *vacuo* at room temperature. The remaining dark-yellow, oily residue was washed several times with petrolether and dissolved in 10 ml absolute ethanol. The ethanolic solution was mixed with 0.71 g (1.7 mmole) $As(C_6H_5)_4Cl$ in 10 ml acetone. Dropwise addition of N_2-saturated water resulted in the precipitation of a yellow solid which was filtered off, repeatedly washed with water and dried for one day at 10^{-3} mm Hg. The pentacarbonyl azido compound obtained in 53% yield contained only very small amounts of $[As(C_6H_5)_4]$-$[W(CO)_5NCO]$ which is characterised by the $\nu_{as}NCO$ absorption in the infrared spectrum at 2230 cm^{-1}.[2,3]

Anal. Calcd. for $C_{29}H_{20}AsN_3O_5W$: C, 46.49; H, 2.69; N, 5.61; W, 24.54. Found: C, 46.46; H, 2.86; N, 5.26; W, 25.54.

Results and Discussion

Kinetic Studies. The second order rate constants of the reaction of $M(CO)_6$ and $N(C_2H_5)_4N_3$ in acetone at different temperatures are recorded in Table I. It may be noted that whereas for M = Cr and W, the k_2 values are constant for different molar ratios of $M(CO)_6$: $N(C_2H_5)_4N_3$ at a particular temperature, for M = Mo the k_2 values decrease slightly with increasing azide concentration. This decrease is certainly not due to a first-order mechanism which parallels the normal second-order path since for a dissociation process according to

$$M(CO)_6 \xrightarrow[-CO]{} M(CO)_5 \xrightarrow{+N_3^-} \text{products} \qquad (2)$$

the activation energy is about 31 kcal/mole[5,6] and the rate constant at 40° $k_1 = 2.7 \times 10^{-8}$ sec^{-1} which is too small to contribute significantly to the observed rate of reaction. The slight decrease of the k_2 values for M = Mo are more reasonably explained by the secondary reaction of the $[Mo(CO)_5NCO]^-$ anion, for example according to Figure 1, which becomes more noticeable with increasing azide concentration. The intermediate formation of a tetracarbonyl anion can be shown by infrared measurements.

The participation of the N_3^- anion in the subsequent reaction steps reduces the effective azide concentration $[N_3^-]_t$ in the reaction with $Mo(CO)_6$ and thus influences the calculation of the second-order rate constants.[7]

Table I. Second Order Rate Constants of the Reactions of $M(CO)_6$ and $[NEt_4]N_3$ in Acetone

M	$M(CO)_6$ [mmole/l]	$[NEt_4]N_3$ [mmole/l]	Temp. [°C]	$10 \times k_2$ [l/mole . sec]
Cr	6.18	24.72	15.0	0.022
Cr	6.18	30.90	15.0	0.018
Cr	6.18	24.72	30.0	0.10
Cr	6.18	30.90	30.0	0.094
Cr	6.18	12.36	40.0	0.295
Cr	6.18	18.54	40.0	0.275
Cr	6.18	24.72	40.0	0.27
Cr	6.18	30.90	40.0	0.23
Cr	6.18	12.36	50.0	0.695
Cr	6.18	18.54	50.0	0.694
Cr	6.18	24.72	50.0	0.65
Cr	6.18	30.90	50.0	0.70
Mo	6.06	18.18	28.5	0.38
Mo	6.06	24.24	28.5	0.31
Mo	6.06	30.30	28.5	0.27
Mo	6.06	18.18	40.0	1.06
Mo	6.06	24.24	40.0	0.93
Mo	6.06	18.18	50.0	2.25
W*	6.08	12.16	18.0	0.40
W	6.08	18.24	18.0	0.44
W	6.08	12.16	30.0	1.09
W	6.08	18.24	30.0	1.05
W	6.08	24.32	30.0	1.065
W	6.08	12.16	40.0	2.32
W	6.08	18.24	40.0	2.21
W	6.08	24.32	40.0	2.27
W	6.08	12.16	50.0	4.26
W	6.08	18.24	50.0	4.05

(*) The k_2 values reported in our previous paper[3] were measured not at t = 28.2° but at t = 26.2°

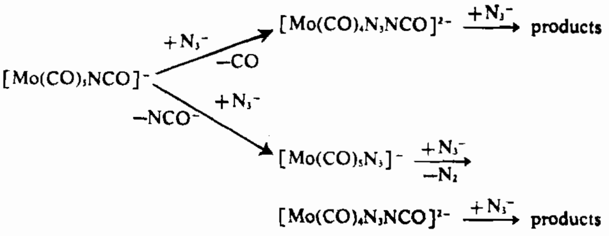

Figure 1.

The activation parameters of reaction (1) are summarised in Table II. For M = Mo, the values of E_a and ΔS^* are put in brackets since they are calculated from the rate constants obtained only for the molar ratio of $Mo(CO)_6$: $N(C_2H_5)_4N_3$ = 1:3. Summation of the kinetic data strongly supports the mechanism outlined in Figure 2.

Although it is impossible to say with any certainty at which position in the starting complex the nucleophilic attack of the azide occurs, it seems most plausible that it is preferably directed to the carbon

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(6) J. R. Graham and R. J. Angelici, *Inorg. Chem.* 6, 2082 (1967).

(7) It may be noted that the azide concentration $[N_3^-]_t$ cannot be determined directly from the infrared spectra in acetone solution for the overlap of the ν_{as} frequency of the free N_3^- anion with the C—O band of the hexacarbonyl. The $[N_3^-]_t$ values are therefore inferred from $[Mo(CO)_6]_t$ by consideration of $[N_3^-]_o$ and the stoichiometry of reaction (1).

Table II. Activation Parameters of the Reactions of $M(CO)_6$ and $[NEt_4]N_3$ in Acetone

M	Temp. [°C]	$10 \times k_2$ [l/mole . sec]	E_a [kcal/mole]	ΔS* [e.u.]
Cr	15.0	0.02		
Cr	30.0	0.097		
Cr	40.0	0.27		
Cr	50.0	0.685	18.8±0.6	−7.8±2.0
Mo	28.5	(0.38)		
Mo	40.0	(1.06)		
Mo	50.0	(2.25)	(15.95±0.8)	(−14.2±2.5)
W	18.0	0.42		
W	30.0	1.07		
W	40.0	2.27		
W	50.0	4.16	13.4±1.0	−20.8±3.0

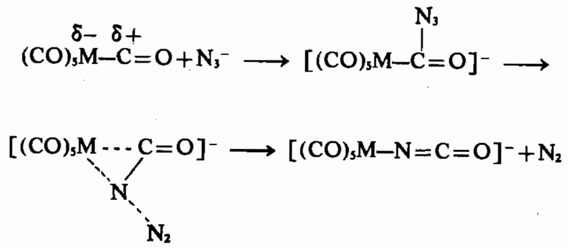

Figure 2.

atom of a CO group. The attack should be facilitated with increasing M–CO distance, which is $Cr < Mo \leqslant W$[8,9] and is the reactivity sequence found in the experiments. At 40°, the relative rates are 1 (Cr): 4 (Mo): 8.4 (W) in accord with the order of the E_a values.

The argument that the increase of the M–CO distance would also support the idea of an attack of the N_3^- anion to the central metal atom cannot be excluded by the kinetic measurements but appears less probable for different reasons:

1. According to recently published MO calculations,[10] the carbon atoms of $Cr(CO)_6$ bear a positive charge of +0.20 and thus are more electrophilic than the central chromium atom of the hexacarbonyl.

2. The reactions of $M(CO)_6$ and N_3^- proceed under very similar conditions as those of the hexacarbonyls with alkyl and aryl lithium compounds.[11,12] The formation of the anions $[M(CO)_5COR]^-$ (which contain a C–R bond) in these reactions is best understood by assuming a nucleophilic attack of the carbanion to the carbon atom of a CO group.

3. The only reaction products obtained from $M(CO)_6$ and N_3^- in acetone, at least for M = Cr and W, are the isocyanato pentacarbonyl anions $[M(CO)_5NCO]^-$. If attack of the azide takes place at the central metal atom, additional formation of the azido compounds $[M(CO)_5N_3]^-$ would be expected. These anions are obviously quite stable as is shown by the preparation of $[As(C_6H_5)_4][W(CO)_5N_3]$.

Thus the first and rate-determining step of the reaction of $M(CO)_6$ and N_3^- may be formulated as shown in Figure 2. The subsequent formation of the M–N bond and the removal of N_2 appear to occur synchronous as is similarly assumed in the Curtius degradation reaction.[13,14] The same « cyclic » transition state is very probably formed also in the reaction of various azido metal complexes with CO to give isocyanato compounds.[1b,15-17]

$$L_mM(N_3)_n + nCO \longrightarrow L_mM(NCO)_n + nN_2 \qquad (3)$$

In this case, kinetic data again support an S_N2-type mechanism.[1b]

Preparative Results. The anion $[W(CO)_5N_3]^-$ originally expected as the product from the reaction of $W(CO)_6$ and N_3^- under *thermal* conditions[2] can be prepared on the *photochemical* route by irradiation of $W(CO)_6$ in tetrahydrofurane and subsequent addition of $N(C_2H_5)_4N_3$.

$$W(CO)_6 + h\nu \xrightarrow[-CO]{THF} W(CO)_5(THF) \xrightarrow[-THF]{+N_3^-} [W(CO)_5N_3]^- \qquad (4)$$

This method (with the intermediate formation of the compound $W(CO)_5(THF)$) has also been used recently by Strohmeier[18] and Guttenberger[19] to prepare various other pentacarbonyltungsten derivatives.

The infrared spectrum of the $[W(CO)_5N_3]^-$ anion (isolated as the tetraphenylarsonium salt) shows the $\nu_{as}N_3$ stretching frequency at 2040 cm^{-1} and three νCO bands at 2076 (A_1), 1914 (E) and 1853 (A_1) cm^{-1}. The positions and intensities of these CO bands are very similar to those of the corresponding isocyanato anion $[W(CO)_5NCO]^-$.[3]

We have also investigated reactions of some other metal carbonyl compounds with azides.[20] Treatment of $Mn(CO)_5Br$ with LiN_3 in tetrahydrofurane at room

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(19) J. F. Guttenberger, *Chem. Ber. 101*, 403 (1968).
(20) H. S. Smedal, Dissertation, Technische Hochschule München, 1965; H. Engelmann, Dissertation, Technische Hochschule München, 1968; W. Beck and K. Joos, unpublished results.

temperature gives a yellow binuclear anion of the analytical composition $[Mn_2(CO)_6(N_3)_3]^-$ as the main product. The rhenium complex $Re(CO)_5Cl$ reacts with NaN_3 in THF at 50° to form the diamagnetic anion $[Re(CO)_3N_3NCO]^-$. The colorless, light-sensitive tetraethylammonium salt yields on reaction with triphenylphosphine in ethanol a mixture of $Re(CO)_3[P(C_6H_5)_3]_2N_3$ and $Re(CO)_3[P(C_6H_5)_3]_2NCO$. Although satisfactory analyses have been obtained for all these compounds, further studies (which are now in progress) are necessary to elucidate their exact structure and the mechanism of their formation. It may be noted that by varying the reaction conditions (temperature, solvent, reaction time) different reaction products are obtained from $M(CO)_5X$ (M = Mn, Re; X = halogen) and azides.

$Co_2(CO)_8$ reacts with $N(C_2H_5)_4N_3$ in water or benzene at room temperature to give both the anions $[Co(CO)_4]^-$ and $[Co(N_3)_4]^{2-}$. Analogously the interaction of $Fe(CO)_5$ and tetraethylammonium azide without solvent yields the tetracarbonylferrate anion $[Fe(CO)_4]^{2-}$ together with an isocyanatoiron complex (possibly $[Fe(NCO)_4]^{2-}$).

In these reactions in which carbonylmetallates are formed the azide may act simply like a reducing agent being oxidised to molecular nitrogen or more probably like a Lewis-base giving rise to a disproportionation, *e.g.*, of 2 Fe^0 to Fe^{II} and Fe^{-II}. It is well known that several Lewis bases containing oxygen or nitrogen as donor atoms react with $Co_2(CO)_8$ and $Fe(CO)_5$ predominantly by disproportionation.[21]

Full details of these and various other reactions of metal carbonyl compounds with the azide anion will be given in a forthcoming publication.

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